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Thin Films of Tin Sulphide for Application in Photovoltaic Solar Cells

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ABSTRACT

Tin sulphide (SnS) is a promising new material for use in photovoltaic solar cells. With a direct energy band gap of about 1.3 eV, and a high optical absorption coefficient, only a few microns of SnS are needed to absorb most of the incident light. Not only is SnS made of abundant, environmentally acceptable elements, it is also amphoteric giving flexibility to device design. Structures that can be envisioned include p-type SnS (absorber layer) / n-type (window layer) heterojunction devices, buried p-n junction devices made using SnS and p-i-n structure devices where the i-layer is SnS. It is most likely that the grain boundaries in SnS can be passivated either by counter-doping the grain boundaries, or by oxidizing the grain boundaries to form wide energy bandgap n-type SnO₂ within p-type SnS, as dopants or oxygen will diffuse preferentially down the grain boundaries and react first at the grain boundary surfaces. Thin film solar cell devices based on the use of SnS have now been produced with efficiencies > 2 %; these and other promising results indicate that it is most likely that devices with efficiencies > 10% will be produced in the near future. Given that tin layers are routinely coated in industry over large area substrates and that industrial sulphidization processes are also well established, the industrialization of this technology should be more straight forward than that encountered with the already commercialised cadmium telluride and copper indium gallium diselenide thin film technologies.

This review discusses the chemical and physical properties of SnS, the methods of producing both bulk crystals and thin films of SnS, the literature available on studies of SnS-

based photovoltaic solar cell devices, and progress made so far in developing this exciting new material.

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1. Introduction

Photovoltaics is universally recognized to be one of the promising ways of sustainably generating electrical power. The most developed photovoltaic solar cells are those based on the use of crystalline or multicrystalline silicon (Si). However with an indirect energy bandgap of 1.1 eV and low optical absorption coefficient, several hundred microns of silicon are needed to absorb most of the incident light. The high material usage and need for high purity silicon in the manufacturing process limit how cheaply such solar cells can be made. Solar cells can also be produced using III–V compounds such as gallium arsenide (GaAs) and indium phosphide (InP). These materials have direct energy bandgaps of 1.4 eV, near the optimum for solar energy conversion. The best cells produced have efficiencies higher than the best silicon devices. They are however substantially more expensive to produce due to the

difficulty in growing high quality crystals of these materials. The high cost limits the number of applications of these devices.

It is now generally recognized that the most promising way to reduce production costs is to use thin films of direct energy bandgap materials. Such layers need to be only a few microns thick to absorb all of the incident light, minimizing materials costs, and expensive production methods can be avoided because most all of the light is absorbed within the junction region, relaxing the need for a long minority carrier diffusion length. Most progress has been made in developing thin film solar cells based on the use of hydrogenated amorphous silicon (a Si:H), cadmium telluride (CdTe), copper indium gallium diselenide (CIGS) [1]. Small area CIGS cells have been developed with efficiencies up to 19.5% and CdTe cells with efficiencies up to 16.5% [2,3]. The technology of these materials has been commercialised and solar modules with efficiencies >12% produced. Fig. 1 shows solar cells produced and sold during 2008 based on the use of different materials [4].

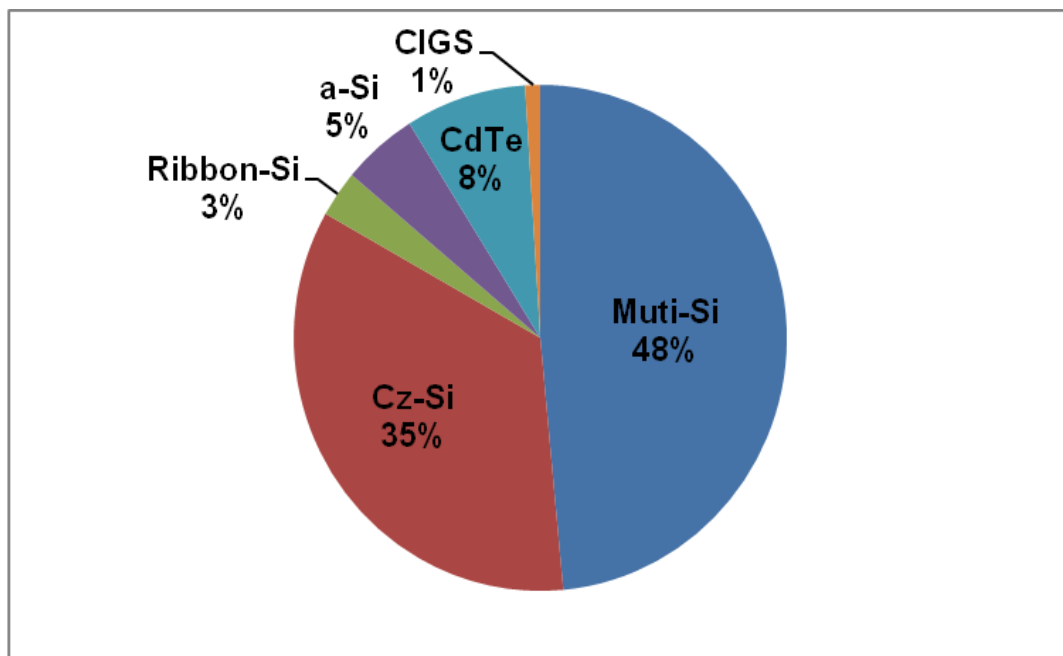


Fig.1. The market share of photovoltaic cell types sold during 2008.

Despite the excellent achievements made with these materials, it is generally recognized that other materials may in the longer term have advantages over these front-runners. In the case of CdTe technology there are concerns with respect to the use of cadmium, which may lead to controlled disposal of modules after use. There are also concerns with the negative perception of the use of cadmium in solar cells by environmentalists. In the case of CIGS a major concern is with respect to the lack of supply of indium and gallium when the technology moves to large scale production. The production of high efficiency cells and modules has also proved to be extremely challenging with this material and related alloys. Currently efforts are being made at various laboratories to develop new solar cell materials to improve the conversion efficiencies either on their own or in tandem structures without these problems. The factors that should be considered in developing novel semiconductor materials for solar photovoltaics include:

- (i) a suitable direct energy band gap that matches the solar spectrum, to maximize absorption of the incident solar radiation,
- (ii) the ability to deposit the material with an acceptable efficiency using a low-cost deposition method such that the “energy payback time” and “energy ratio” are acceptable,
- (iii) abundancy of the elements involved and
- (iv) there are low “environmental costs” when a “cradle to grave” lifecycle analysis is made with respect to the extraction of the elements, use of thin film production methods, operation of modules and disposal of modules.

Tin monosulphide (SnS) is one of the promising materials that satisfy the above criteria. It is now receiving attention due to its potential use not only in photovoltaic cells, but also for holographic recording, solar collectors and heat mirrors. SnS has a direct energy band gap of about 1.3 eV and a high optical absorption coefficient ($> 10^4 \text{ cm}^{-1}$) which means that only a

few microns of material are needed to absorb all of the incident light [5, 6]. The constituent elements Sn and S are abundant and non-toxic and SnS can be doped with both n-and p-type conductivity types, the electrical properties controlled by either by altering the stoichiometry of the compound or by extrinsic doping with suitable elements e.g. Ag, Al, N and Cl [7, 8]. It is also possible that the CdS, ZnS and other II–VI compounds used as window layers in CdTe and CIGS solar cells may be suitable partner materials for p-SnS.

2. Material Properties

Tin forms a range of sulfides which include SnS, SnS₂ and Sn₂S₃. Among these, SnS and SnS₂ are the most widely studied materials. These have energy band gaps of 1.30 and 2.18 eV respectively [9, 10]. Tin sulphide, in the form of small (“bulk”) crystalline/multicrystalline ingots, have been synthesized from the elements, from molecular precursors, by solid state metathesis and by the reaction of H₂S with metal oxides. There are numerous reports of forming single crystals of SnS₂ via the vapor transport method.

Tin monosulphide (SnS) belongs to the IV–VI group of layered semiconductors. It is also known as herzenbergite in honour of the the German mineralogist R. Herzenberg who first investigated this material [11]. SnS crystallizes in orthorhombic crystal structure wherein each tin atom is coordinated by six sulfur atoms. There are three short Sn-S bonds with an interatomic spacing of 2.7 Å and three long Sn-S bonds with an interatomic spacing of 3.4 Å. Fig.2 shows the layered structure of SnS. There are two SnS layers in one unit cell and one of the long distance sulfurs actually resides on the neighboring SnS layer. Within a layer the Sn-S bonds are strong while the two neighbouring layers are bonded by weak van der Waals forces [12]. This weak Sn-S interaction binds the two tin sulfide layers together in a unit cell to form a double-layer structure. However, the van der Waals forces provide a chemically inert surface leading to higher chemical stability that avoids photocorrosion in the fabricated

devices. Tin monosulfide undergoes a complicated thermal expansion from room temperature to 605 °C at which it transforms to tin disulfide type structure [13]

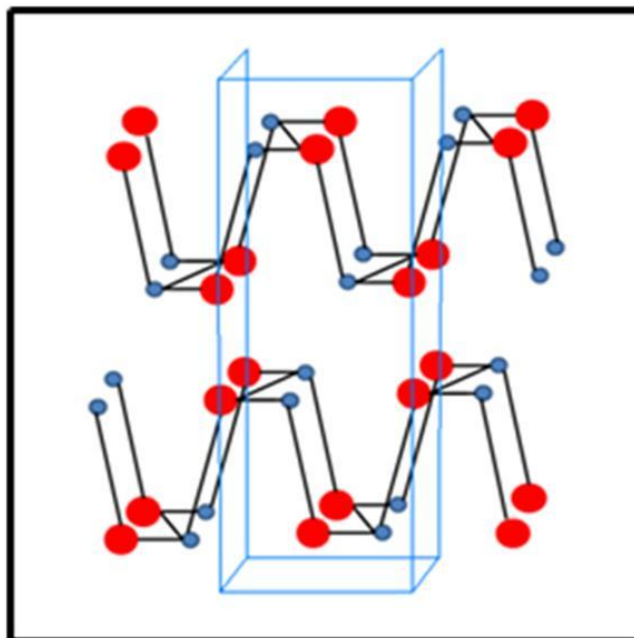


Fig.2. Layered crystal structure of SnS (● represents S and ● represents Sn atoms)[14].

It is important to have knowledge of the solid-liquid-gas phase equilibrium of the Sn-S system, particularly in the region of SnS compound in order to understand the formation of various phases of Sn and S and to grow crystals under controlled conditions. Fig.3 shows the Temperature-Composition (T-x) diagram of the Sn-S system, which shows that the two prominent phases, SnS and SnS₂ melt congruently [15]. The melting points of these compounds were found to be 882°C for SnS and 870°C for SnS₂. Studies on the phase transformation in SnS revealed that it shows a structural transition from a less symmetric α -phase at low temperatures into a symmetric β -phase for temperatures > 878 K. The $\alpha \rightarrow \beta$ phase transition is considered as second-order transition, which is produced by a continuous shift of Sn and S atoms along the [100] axis [16].

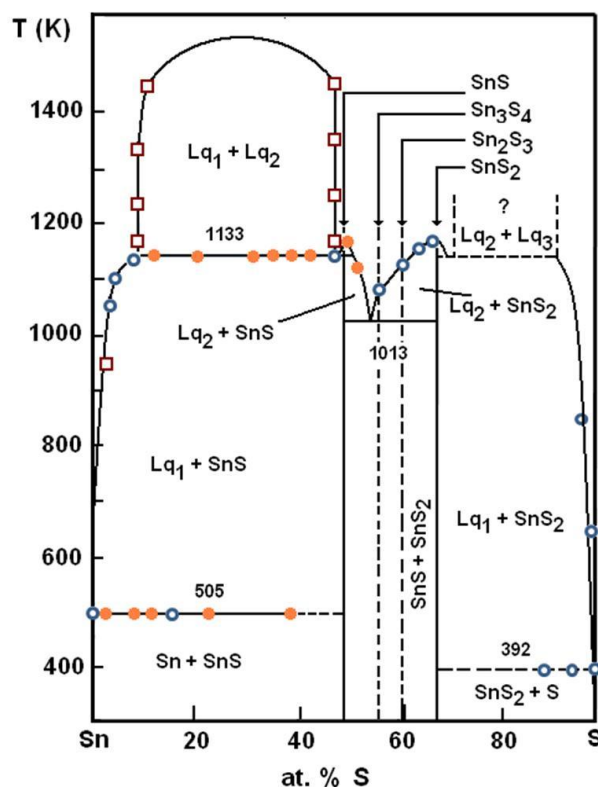


Fig.3. Temperature versus S-composition (T vs x) phase diagram for Sn-S system [17].

Bulk tin sulfides have been synthesized from the elements [18], from molecular precursors[19], by solid state metathesis [20] and by the reaction of H_2S on metal oxides [21]. Conventionally, SnS and SnS_2 single crystals have been prepared by direct vapor transport technique [22], the stoichiometric composition technique [23], by physical vapor transport (PVT) method [24] and using the Bridgman-Stockbarger technique [25]. Solvo-thermal methods, using a combination of tin chloride and thiourea or elemental Sn and S, have produced 0-D spherical particles or 1D whiskers with the orthorhombic crystal structure.[26, 27]. For different synthesising conditions different crystallographic structures have been reported. Greyson et al. report the growth of 3D tetrahedral crystals of SnS with the zincblende (sphalerite) crystal structure and achieved a morphological yield greater than 90%. 2D plates of SnS with an orthorhombic structure have been produced by increasing the reaction temperature [28].

3. Film Deposition Methods

Work on SnS films was mainly initiated by Engleken and others using chemical precipitation and electrodeposition methods [29-33]. This was followed by the synthesis of these films by other methods such as chemical bath deposition [34-36], electrodeposition [37-39], electrochemical deposition [40, 41], spray pyrolysis [42-47], brush plating [48], close spaced vapor transport [49], sputtering [50], molecular beam epitaxy [51], electron beam evaporation [52], SILAR (Successive Ion Layer Adsorption and Reaction) method [53], sulphurisation of metal layer [54-56] and vacuum evaporation [57-59]. These films were also fabricated using chemical vapour deposition methods such as atmospheric pressure chemical vapour deposition (APCVD), low pressure chemical vapour deposition (LPCVD), plasma enhanced chemical vapour deposition (PECVD) and aerosol assisted chemical vapour deposition (AACVD) [60-63]. A brief description of these techniques are given in the following sections.

3.1. Chemical bath deposition

Chemical bath deposition (CBD) is a simple process used to synthesize thin films of a wide range of materials [64-66]. It can also be referred to as solution growth method. In recent years this technique has been used extensively to deposit buffer layers for photovoltaic solar cell application. The technique is based on the kinetically controlled reaction between constituent ions. It involves the controlled precipitation from solution of a compound onto a suitable substrate. Fig. 4 shows the schematic of a typical CBD system used for the synthesis of CdS and SnS films. A soluble salt of the required metal is dissolved in an aqueous solution, to release cations. The non-metallic element is provided by a suitable precursor compound, which decomposes in presence of hydroxide ions, releasing the anions. The anions and cations then react to form the compound. Generally SnS deposition in CBD is carried out using the

constituents: (1) a tin precursor: SnCl_2 or SnCl_4 (2) a sulfur precursor: $\text{Na}_2\text{S}_2\text{O}_3$, trethanolamine or thioacetamide and (3) a complexing agent, which is commonly ammonia.

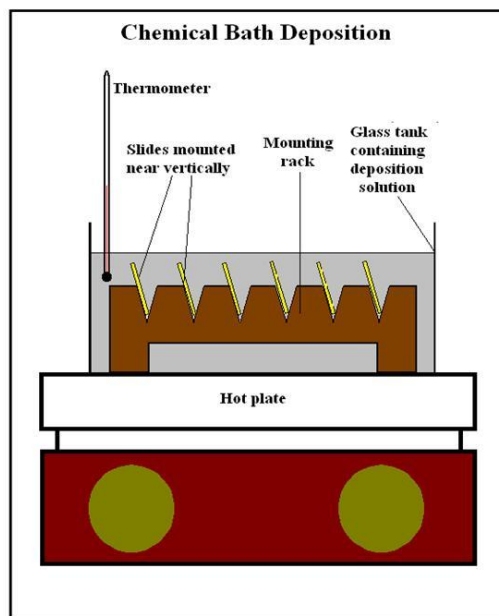


Fig. 3.1. Chemical bath deposition system

After immersing the substrates in the solution, the bath is heated to the desired temperature, usually $60 - 80^\circ\text{C}$. This is to improve the surface morphology of the deposited layer. Films produced in this process have a rough topology, resulting in low optical transmittance. In order to minimize this, a complexing agent, mostly ammonia, is used to form complex ions with the metal ions. This exists in equilibrium with ammonium hydroxide, which also provides the hydroxide ions for decomposition of thiourea. The ammonia used in most recipes is considered to be crucial for cleaning of the absorber surface and removal of oxides and impurities. The Sn-complex ion and the sulphide ion migrate to the substrate surface, reacting together to form SnS . Layers grown by this process are dense, homogeneous and uniform over the substrate. The growth parameters such as film thickness and deposition rate can be controlled by varying the solution pH, reagent concentration and temperature

3.2. Thermal Evaporation

Thermal evaporation is one of the simple vacuum deposition techniques where the source material is evaporated from an evaporation source / effusion cell in high vacuum by heating the source material. The deposition rate and uniformity of the vapor species arriving at the substrate are controlled by the source temperature, the geometry of the source, the source-substrate distance and the vacuum in the chamber. Evaporation using effusion cells provide a precise control over the beam distribution and utilization. Fig. 5 shows the thermal evaporation process for the deposition of thin films.

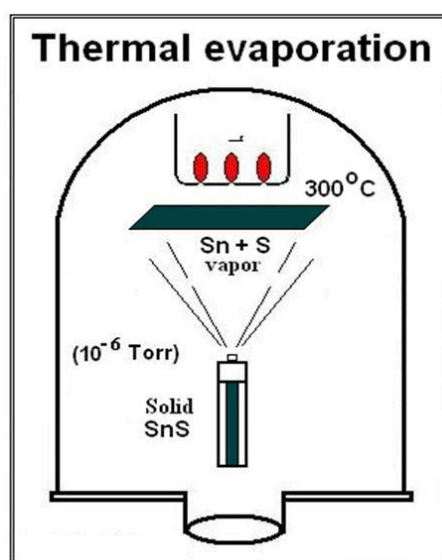


Fig. 5. Thermal evaporation technique.

Typical source and substrate temperatures used for the preparation of SnS layers were in the range, $300\text{-}600^{\circ}\text{C}$ and $100\text{-}400^{\circ}\text{C}$ respectively [66]. The source-substrate distance used by various researchers varied from few cms to several cms. The layers grown at this temperature are usually crystalline, conformal, homogeneous and free from pin holes.

3.3. Sputtering

Sputtering is a rapid deposition process, which can be easily scaled-up for industrial production. SnS films have been deposited by radio-frequency magnetron sputtering using the compound target with Ar as the sputter gas [67]. In this case the mass transfer of Sn and S occurs via sputtering of SnS target, diffusion of these atoms onto the substrate surface followed by condensation. The energetic ionized sputter gas atoms form the plasma that strike the target and remove the material atoms. These atoms consequently deposit on the substrate, placed on the counter electrode facing the target forming the film. Fig. 6 shows the pictorial representation of sputter deposition process.

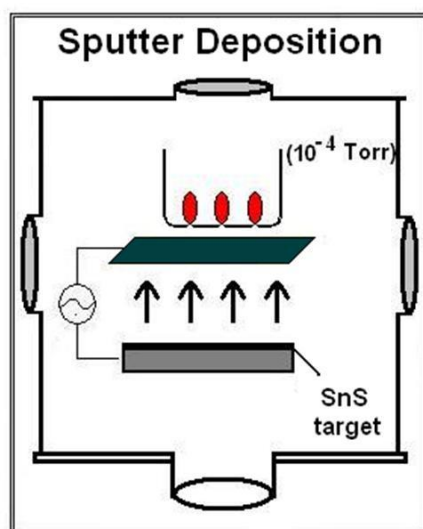


Fig. 6. Sputter deposition process.

The deposition is carried out using substrate temperatures of 200-350°C and at a sputter pressure of $\sim 5 \times 10^{-2}$ Torr. The layers were deposited at a typical deposition rate of 3-5 Å/sec. The rf power, anode voltage and anode current were varied in the range, 30-70 W, 0.5-1.4 kV and 30-80 mA respectively. Pure Ar was used as the sputter gas [248].

3.4. Spray pyrolysis

It is a non-vacuum technique that can be used for industrial production by using linear nozzle arrays inline system. An aerosol of water droplets containing the compounds of the constituent elements that are heat decomposable are sprayed onto heated substrates. The droplets on reaching the substrate surface undergo pyrolytic decomposition, followed by reaction among the ions leading to the formation of the required compound in solid form. Fig. 7 shows the schematic of spray deposition system.

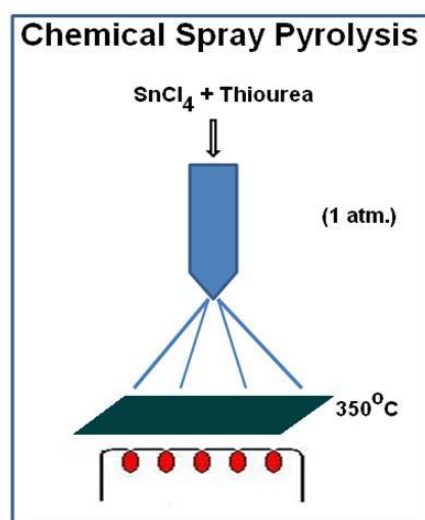


Fig.7. Chemical Spray Pyrolysis set-up.

This technique has been used effectively for the growth of oxides and chalcogens of various metals [68-73]. To deposit SnS layers using this process, Sn-precursors such as SnClO₄ and SnCl₄ are mixed with thiourea solution and then sprayed using N₂ as the carrier gas [46, 47]. The substrate temperature (T_s), solution concentration (S_c), solution flow rate (R_s), air flow rate (R_a) and source-nozzle distance (D_{s-n}) are the important deposition parameters that control the quality of the layers. The layers grown by this technique are well adherent to the substrate surface, uniform and pin-hole free.

3. 5. Electrodeposition

It is one of the economic chemical process that can be used for large are thin film deposition [74]. The electrodeposition of II-VI compounds has been widely studied, mostly for the synthesis of tellurides, selenides and sulfides. Biased (either dc or pulse) electrodeposition is found to improve the morphological and optoelectronic properties of the layers than the normal electrodeposition [75, 76]. In pulsed electrodeposition, a three-electrode cell was used with a saturated calomel electrode (SCE) as the reference electrode, an indium–tin oxide (ITO) coated glass as the working electrode, and a platinum sheet as the counter electrode. Electrochemical deposition (ECD) and photoelectrochemical deposition (PECD) methods are also used to produce SnS layers where the equipment in these processes was the same with a change in the precursors used. In addition, in PECD system the sample was illuminated with a Xe lamp of 100 mW/cm^2 intensity. Fig. 8 shows a schematic of two electrode electrodeposition system.

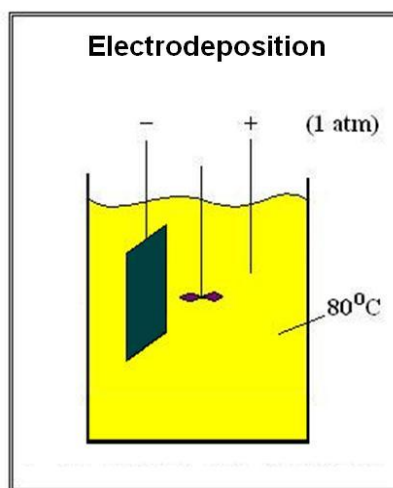


Fig. 8. Schematic of electrodeposition system.

In a typical deposition, the precursors used were 20 mM SnSO_4 and 100 mM $\text{Na}_2\text{S}_2\text{O}_3$ [75]. In that the pH of the solution was adjusted to 1.5–4.0 by adding H_2SO_4 and the bath temperature was kept at room temperature. The current density during deposition was varied

in the range, 1-5 mA/cm², and the deposition time was ~ 1.5 h. The films grown by this process are smooth, pin hole free and strongly adherent to the substrate surface.

3. 6. Chemical vapour deposition (CVD)

Chemical vapour deposition involves passing a mixture of gases over a heated substrate where they chemically react to form a layer of material on the substrate surface. The temperature at which they react can be reduced by carrying out the process in a plasma, in which case the process is known as plasma enhanced chemical vapour deposition (PECVD). SnS layers have been deposited using APCVD and PECVD processes using gaseous precursor reactants such as SnCl₄ for Sn and H₂S to carry the sulphur [77, 78]. In the reactor chamber, they are subjected to time-varying electric fields. Inelastic collisions between energetic electrons and gas molecules generate highly reactive species that are adsorbed on the substrate surface. If the substrate is heated to an appropriate temperature, then the desired chemical reaction take place and the desired films is deposited on the substrate surface while the reaction byproducts are pumped out of the system. Fig. 9 shows the schematic of a PECVD system.

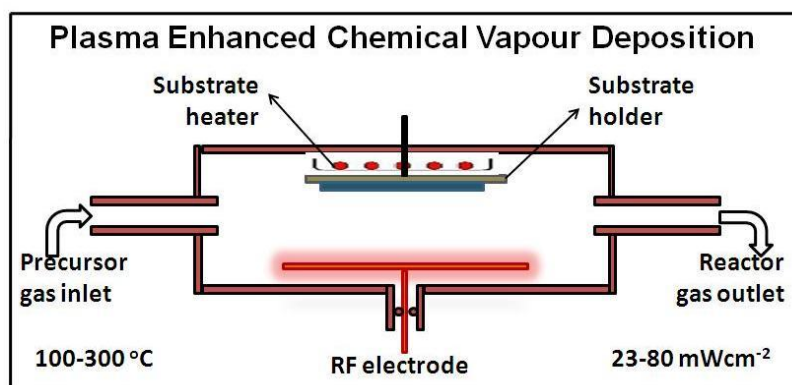


Fig. 9. Schematic diagram of a PECVD system.

The substrate temperature and rf plasma power density for the latter process typically varied in the range, 100-300 °C and 0.023-0.080 Wcm⁻² respectively. The interelectrode distance was 3.0 cm. Hydrogen was used as a dilute gas to remove the chlorine radicals [62].

3.7. Sulphidisation Process

This is a simple, economic two-stage process that can be used to grow metallic sulphides over large areas. It has been extensively used in the production of CuInGaSe_2 films for application in photovoltaic solar cells and the technology has been commercialised. In this process thin layers of metals are coated on the substrate using a thin film deposition method e.g. thermal evaporation, sputtering or electrodeposition and the layer then converted into the compound by heating them in the presence of H_2S gas or elemental sulphur. Fig. 10 shows a schematic view of a typical single zone sulphidisation furnace. Either H_2S gas is passed over the heated metallic thin film or sulphur is incorporated with the sample in a graphite box, argon passed through the system to drive out the air, and the box then heated. The zone temperature (s) and the sulphidization time period are the important growth parameters that control the formation of metal sulphides.

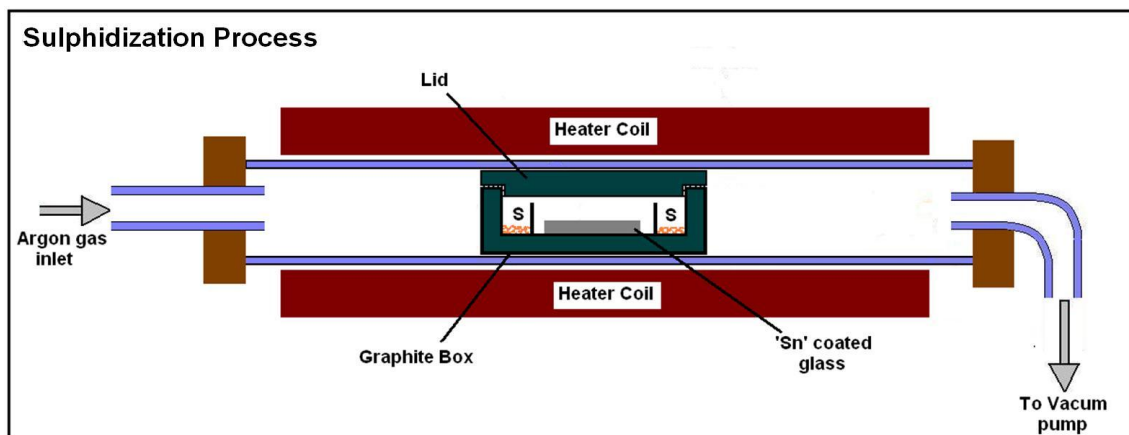


Fig. 10. Schematic of sulphidization furnace.

Typical temperatures that used for sulphidization for using a graphite box varied in the range, 100-400°C for a time period of 20 min [79]. Minemura et al. used low sulphidized temperatures of 120-220°C, but with longer time periods of 60 min [80].

4. Properties of SnS films

The chemical and physical properties of Sn/S films deposited have been found to depend strongly on the growth technique used and on the precise deposition conditions used with that growth method. The films deposited are often found to consist of a mixture of the different phases of Sn and S e.g SnS₂, SnS and Sn₂S₃ (and sometimes SnO₂ if they are exposed to air at elevated temperatures). X-ray diffraction data taken on the SnS films grown using most of the techniques indicates that SnS is deposited with the orthorhombic crystal structure with (111) as the preferred orientation, although a few other workers have reported (040) orientated layers instead. The optical energy band gap has been reported to be in the range, 1.0 – 1.7 eV depending on the deposition method and deposition conditions used. There is however a general consensus from the more detailed studies that the energy band gap of SnS is 1.3 – 1.4 eV, higher values being due to the presence of other phases of Sn and S or SnO₂. The less reported values, < 1.3 eV are not understood, but may be associated with the very thin layers of Sn and S used in these early studies. The films have electrical resistivities that vary from 5 Ωcm to 10⁵ Ωcm with associated carrier concentration that also vary over three orders of magnitude, from 10¹⁴ cm⁻³ to 10¹⁷ cm⁻³. Carrier mobilities as high as 500 cm²V⁻¹s⁻¹ have been reported in some studies. Most of the films deposited are found to be photoconductive, for wavelengths ranging from the near infrared to the ultraviolet region [81].

SnS layers grown by the chemical precipitation method with the solution containing < 10 % H₂O had a predominantly Sn_{1-x}S phase that exhibited an indirect band gap of 1.0-1.3 eV. Further, the films deposited without H₂O in the solution exhibited Sn_{2-x}S₃ while those layers grown with potassium gluconate and tartaric acid in the solution had SnS_{2-x} phase with an optical band gap of 2.1-2.3 eV [31]. Partin et al. deposited SnS films by chemical vapour deposition where the films had SnS₂ phase for a growth temperature of 350°C, Sn₂S₃ at 400°C and only SnS phase for temperatures > 500°C [82]. A similar change of phases with

substrate temperature was also observed in APCVD grown layers [77]. A change in the preferred orientation from (111) to (040) was reported by Noguchi et al. where the layers deposited by evaporation for temperatures $< 200^{\circ}\text{C}$ showed (111) plane while those grown above 280°C had (040) plane as the preferred orientation [57]. However, SnS films deposited by thermal co-evaporation and molecular beam epitaxy showed (040) as the preferred orientation [83, 51].

The Hall measurements conducted on the films deposited by different techniques revealed p-type electrical conduction. However, n-type electrical conduction was observed in chemically deposited films when annealed at temperatures $> 200^{\circ}\text{C}$ in air and Ar [34, 84, 50]. Evaporated layers showed the highest Hall mobility of $500\text{ cm}^2/\text{Vsec}$ with a carrier concentration of $\sim 10^{14}\text{ cm}^{-3}$ while the films deposited by close spaced vapour transport exhibited a low mobility of $3.7\text{ cm}^2/\text{Vsec}$ with the highest carrier density, $\sim 10^{17}\text{ cm}^{-3}$. Films prepared by other techniques have their Hall mobilities and carrier concentration in between these values. Arrhenius plots of the resistivity have also been used to determine an activation energy for the conduction process; this varied from 0.25 eV to 0.70 eV depending on the growth technique used.

The influence of substrate temperature, film thickness, substrate surface and annealing on the physical properties of evaporated SnS was investigated by Devika et al [59, 85-88]. They reported that substrate temperatures $\geq 275^{\circ}\text{C}$ could be used to produce films with a energy band gap of 1.35 eV with an electrical resistivity of $34.5\text{ }\Omega\text{cm}$. SnS layers grown on ITO coated glass had a lower resistivity ($4.7\text{ }\Omega\text{cm}$) compared to that obtained for SnS layers deposited on glass, Si wafer and Ag-coated glass; these layers had a wider energy band gap (of 1.55 eV). Further the layers grown on Si wafer showed (040) as the dominant peak while those on other substrates had the (111) plane as the preferred orientation. Fig. 11 shows the AFM pictures of SnS films deposited on different substrates grown at a temperature of 300°C

with a thickness of 0.5 μm . Films that were grown on glass and ITO exhibit clear and uniform morphology while those grown on the Si wafer and Ag-coated glass substrates had irregular surface structure with higher surface roughness.

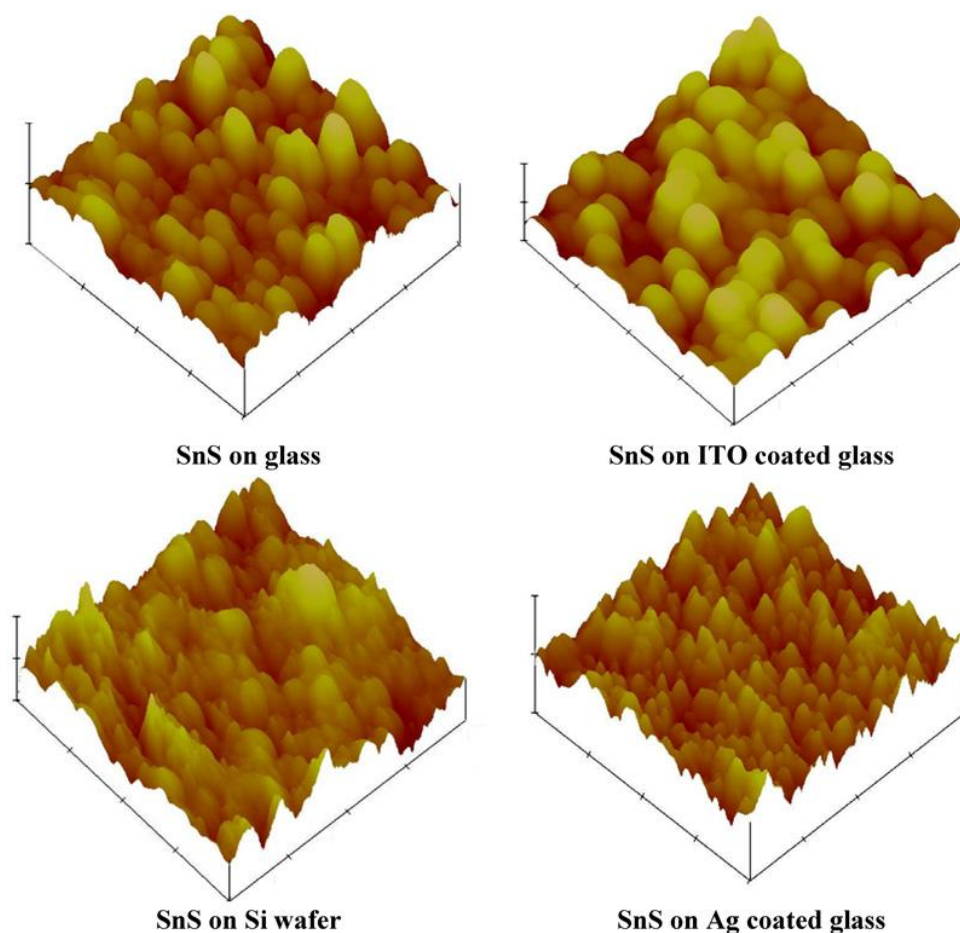


Fig. 11. AFM pictures of SnS films grown on different substrates at 300°C.

Deraman et al. studied the effect of substrate temperature on the chemical and physical properties of thermally evaporated SnS layers [89]. They found that the layers grown at temperatures $< 200\text{ }^{\circ}\text{C}$ were non-stoichiometric and that other Sn/S phases, SnS_2 and Sn_2S_3 , were present. They also concluded that the dominant conduction mechanism was due to hopping of carriers via localised states.

The effects of source temperature, substrate temperature and film thickness on the chemical and on the physical behaviour of SnS films deposited using vacuum thermal evaporation were investigated by Ogah et al [90, 91]. They found that if the source temperature was kept constant, then the ratio of Sn/S in the deposited layers varied from Sn-rich for a substrate temperature of 100°C, to stoichiometric for a substrate temperature of 360 °C and then S-rich for higher substrate temperatures. Fig.12 shows the X-ray diffraction spectrum of SnS film deposited at a source temperature of 300°C with a substrate temperature of 300°C. They also found the energy band gap dropped with an increase in film thickness, it tending to 1.3eV for film thickness > 1 µm; and increasing to > 1.6 eV for film thickness < 0.5 µm. They interpreted the wider band gap due to alloying of Sn₂S₃ with SnS. They also pointed out that Sn₂S₃/SnS alloys may have potential for use as absorber layers in thin film solar cells as they have near optimum energy band gap required.

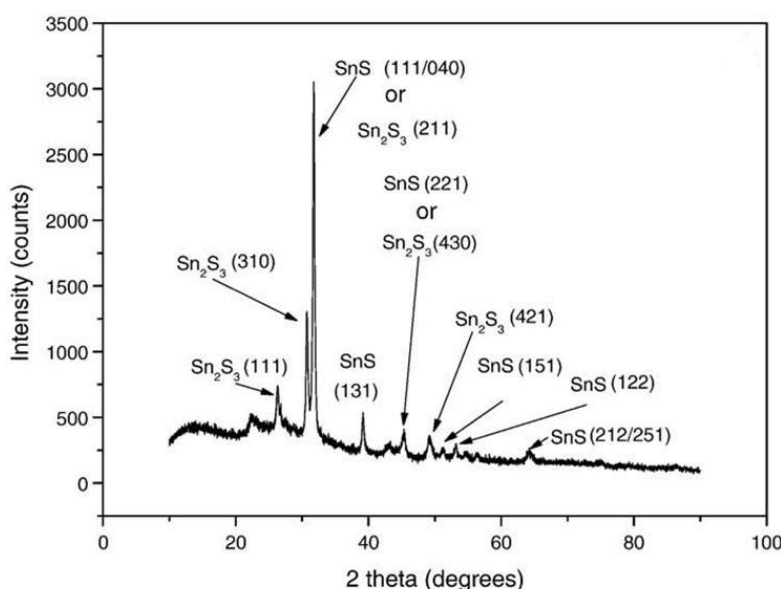


Fig. 12. X-ray diffraction spectrum of SnS grown by evaporation.

Films of SnS can also be deposited by chemical bath deposition using stannous chloride and sodium thiosulphate pentahydrate as precursor materials. The films were found

to have an optical energy band gap of 1.0 eV [92]. The films were found to be highly resistive, p-type with an Arrhenius activation energy for conductivity of 0.62 eV.

Single phase SnS films have been prepared by the simple two-step process, involving the deposition of a thin layer of tin followed by sulphidization [79]. The process involved the deposition of the Sn layer on a soda-lime glass substrate using dc magnetron sputtering followed by its conversion into SnS by annealing in presence of elemental sulphur at different temperatures. The films annealed at temperatures in the range, 300-350°C were stoichiometric with a strong (111) orientation and exhibited the (111) plane as the preferred orientation. These films had an electrical resistivity of $1.5 \times 10^{-2} \Omega\text{cm}$ with an optical energy band gap of 1.35 eV. However, the layers synthesised at temperatures $< 300^\circ\text{C}$ contained SnS_2 and Sn_2S_3 in addition to SnS while those formed at temperatures $> 350^\circ\text{C}$ had SnS_2 along with SnS phase. There are also reports on the synthesis of SnS by sulphidising Sn sheet using temperatures in the range, 150-200°C [80]. The films synthesized at 170°C showed the (111) plane as the predominant orientation. The optical band gap of these layers was found to be 1.3 eV.

Chemical spray pyrolysis has also been used to deposit SnS films. The layers were deposited using SnCl_4 and thiourea as precursors with a solution concentration of 0.1 M. Lopez et al. reported single SnS phase at 390°C with an indirect optical band gap of 1.3 eV [42] while Thangaraju et al claimed a band gap of 1.0 eV for those deposited at 350°C [44]. However, a direct optical band gap of 1.32 eV was reported by Reddy et al. for the layers deposited at 350°C whereas those formed at lower and higher temperatures had a higher energy band gap [43]. Fig. 13 shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ drawn for SnS films grown at different temperatures in this study. The films exhibited a strong (111) orientation, and they had an electrical resistivity of 30 Ωcm with a net carrier density of $2 \times 10^{15} \text{ cm}^{-3}$.

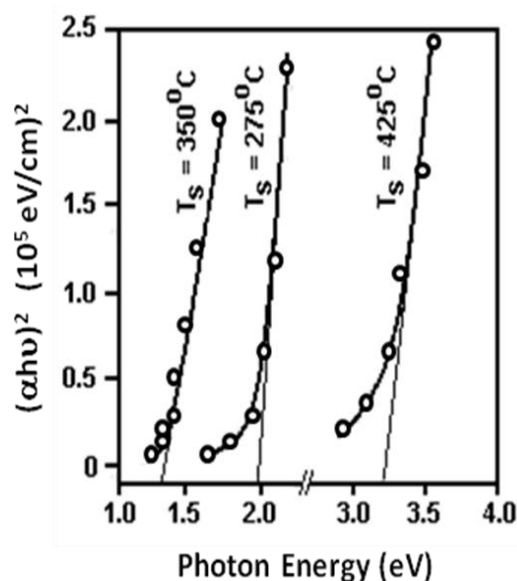


Fig. 13. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for SnS films grown by spray pyrolysis.

Uniform and photoactive films of SnS have been deposited by electrodeposition from an aqueous medium. These films were nearly stoichiometric. Electrically they were found to be p-type and photoconductive when illuminated with white light. [37, 74, 93]. The thermal stability of dip coated SnS and SnS₂ films were studied by Ray et al. The energy band gap values obtained from photoconductivity measurements were 1.4 and 2.4 eV for SnS and SnS₂ films, respectively. Annealing the films in air at 400°C converted both SnS and SnS₂ films to the transparent conducting oxide, SnO₂ (tin dioxide). Vacuum evaporated films were also found to be photoconductive which increased during annealing in air. The increase in photoconductivity was interpreted as due to the thermal activation of oxygen acceptors with annealing. As with the dip coated films the SnS layers were converted to SnO₂ if annealed for long enough at a high enough temperature. The films were photoconductive for incident light with wavelengths from the near-infrared to the ultraviolet part of the spectrum. A more detailed study of how the chemical and physical properties of thicker layers of tin sulphide (0.5µm- 3µm) deposited using vacuum evaporation has also been made [95]. In this study the

way the properties varied with source temperature, substrate temperature and film thickness deposited were investigated.

SnS layers have been grown on titanium substrates using cathodic electrodeposition, by Ghazali et al [74]. The presence of EDTA in the deposition bath was found to improve the adhesion of the film on titanium substrates significantly. The structural and optical properties of SnS films deposited by pulse electrodeposition have also been investigated by Yue et al [75]. The films were found to have an energy band gap of 1.34 eV and had the (040) plane as the preferred orientation. SnS films have been produced by electrochemical deposition by Sato et al. and the I-V behaviour of the different elements investigated. They found that Au and In are Ohmic while Al forms a Schottky contact [76]. The layers were also found to be photocoductive. Nair et al. investigated the conversion of chemcially deposited SnS layers into SnO₂ [96]. SnS films annealed for temperatures > 325°C were converted into transparent SnO_{2-x} layers. These films had a sheet resistance of 10⁴ Ω/□; this increased to 10⁹ Ω/□ upon annealing at 500°C for 18 hrs.

Thin films of SnS have been grown using APCVD (atmospheric pressure chemical vapour deposition) and by using PECVD using tri-*n*-butyltin trifluoroacetate and H₂S as the reactant gases for the APCVD and SnCl₄ and H₂S for the PECVD [60, 62]. All the SnS films deposited were found to have the orthorhombic crystal structure for the range of deposition conditions used in their study. The energy bandgap of all the layers was found to be 1.16 eV and the films *p*-type conducting with an activation energy of 0.3 eV. Good quality tin sulfide thin films have also synthesised from single-source precursors, [Sn(SCH₂CH₂S)₂] on glass substrates by aerosol-assisted chemical vapour deposition in the presence of H₂S. The films deposited were found to mixtures the different polymorphs of tin sulphide, SnS, SnS₂ and Sn₂S₃, the precise mixture depending on mainly on the substrate temperature used. The energy band gap for SnS and SnS₂ were found to be 1.15 eV and 2.20 eV, respectively. Some efforts

have been made to make Ohmic contacts to SnS films. Ghosh et al. [97] studied the barrier characteristics and stability of indium, aluminium, copper and silver contacts to SnS films. Indium was observed to form an Ohmic contact to p-SnS for all the annealing conditions. The other three metals act as Schottky diodes. Although aluminium formed a Schottky contact to polycrystalline SnS, annealing at 350 C rendered it Ohmic [98].

Recently, research on nanostructured SnS thin films and bulk materials has been intensified due to its potential application in electronic, optical and superconductor devices. The fundamental properties of these nanostructured SnS material depends on its architectures including geometry, morphology and hierarchical structures. The control of the shapes and sizes to get the desired properties is one of the most challenging issues to be considered [99-102]. Nanocrystalline SnS has been synthesised by solvothermal/ hydrothermal procedure with tin salts as precursors. The different polymorphic forms of tin sulfide (SnS, SnS₂, Sn₂S₃ etc) have been crystallised by a solvothermal route where tin foils were used as the source of Sn instead of tin salts [103]. This recently developed method is believed to be a promising method to control the synthesis of materials, where the polymorphs are very sensitive to the reaction conditions, due the chemistry being conducted at much lower temperatures than usual [104, 105]. This technique has been successfully applied to the synthesis of a variety of nanoscale semiconductors [106, 107].

5. SnS-based Solar Cells

The photovoltaic potential of SnS layers was initially observed in photo-electrochemical (PEC) cells. The SnS layers, grown by different chemical routes, were used as photocathodes in the PEC cells. Conversion efficiencies > 0.5 % with fill factors > 0.6 were observed for such devices [108]. Research into using vacuum evaporated SnS thin films as an absorber in CdS/SnS heterojunction solar cells was initiated in 1994. For these devices, an

open circuit voltage (V_{oc}) of 120 mV, a short circuit current density of 7 mA/cm^2 and a conversion efficiency, $\eta = 0.29 \%$ were reported [57]. This work initiated interest in this material. In 1995 Reddy et al. produced an Al/CdS/SnS/Ag cell structure with improved J_{sc} (8.4 mA/cm^2) and produced the device with an improved efficiency (0.5%). For these cells the SnS layers were produced using the spray pyrolysis method [109]. Fig. 14 gives a schematic cross section of a typical n-CdS/p-SnS solar cell structure. The current transport across the junction modelled as a composite of tunneling and recombination mechanisms.

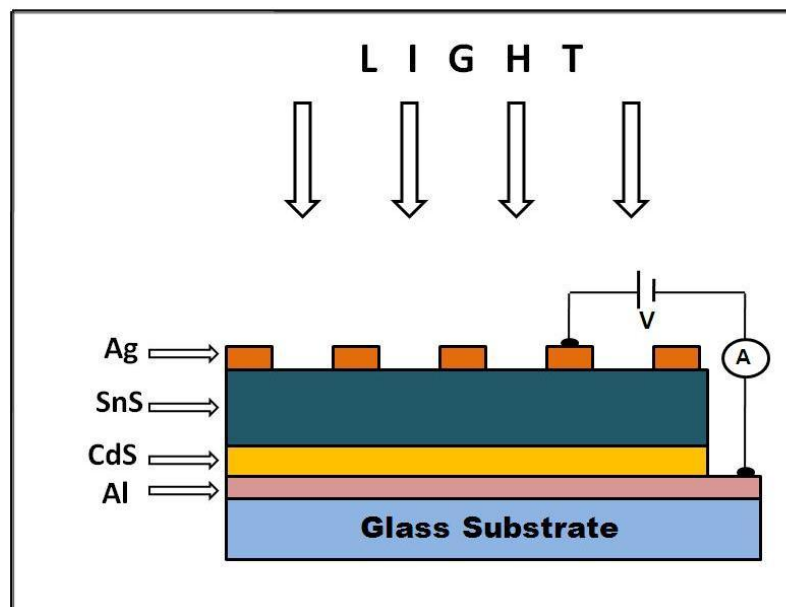


Fig. 14. Schematic of the SnS-solar cell structure.

Table 1 gives the photovoltaic parameters of SnS-based solar cells that have been developed using different window layers. It should be noted here that the parameters listed in the table have been recorded on junctions using the SnS films deposited using different methods and the efficiencies measured using different values of light intensity. Table 2 lists the deposition methods used for the fabrication of SnS and CdS layers and the reported solar cell parameters on CdS/SnS structures. Ristov et al. developed CdO/SnS, $\text{Cd}_2\text{SnO}_4/\text{SnS}$ and

SnO₂:F/SnS junctions using chemically deposited SnS layers [110]. The cells made with CdO and Cd₂SnO₄ had values of V_{oc} , > 200 mV, while the cell with SnO₂:F as window showed a maximum response in the ultraviolet region with a lower V_{oc} value. However, the observed J_{sc} values were very low in these junctions. Electrodeposited SnS layers were used by Subramanian et al. to develop a photoelectrochemical cell with the configuration p-SnS|Fe³⁺, Fe²⁺|Pt. These cells had open circuit voltages > 320 mV with short circuit currents < 1 mA/cm² [108]. P-SnS/n-SnS₂ heterojunctions were made using the SnS and SnS₂ layers grown by PECVD on TCO coated glass. The junctions had an open circuit voltages up to 0.35 V. However, the device efficiency was limited to < 1 %, due to low value of J_{sc} (1.5 mA/cm²) [111]. The devices also had a high series resistance and a small shunt resistance with a reverse saturation current density of 1.2×10^{-5} A/cm².

Table 1 : Photovoltaic parameters of SnS-based junctions using various window layers.

Window Material	V_{oc} (mV)	J_{sc} (mA/cm ²)	Fill Factor	Efficiency, η (%)	Ref.
Si	480	8.76	0.50	0.7	[112]
CdS	500	10.0	0.50	2.5	[113]
ZnS	135	0.95	---	---	[114]
CdO	200	0.54	---	---	[110]
ZnO	380	0.08	0.40	---	[115]
SnS ₂	350	1.50	---	---	[111]
SnO ₂ :F	152	0.12	---	---	[110]
Cd ₂ SnO ₄	230	0.04	---	---	[110]
CdZnS	288	9.16	0.27	0.71	[116]

Table 2 : Photovoltaic parameters of differnt SnS/CdS solar cells.

SnS growth technique	CdS growth technique	V _{OC} (mV)	J _{SC} (mA/cm ²)	Fill Factor	Efficiency, η (%)	Ref.
Chemical bath deposition	Electrodeposition	200	13.2	0.31	0.81	[112]
Electrochemical deposition	Photochemical deposition	170	3.3	0.37	0.20	[116]
Chemical bath deposition	Chemcial bath depostion	340	6.0	--	--	[117]
Vacuum evaporation	Vacuum evaporation	120	7.0	0.35	0.3	[57]
Spray pyrolysis	Vacuum evporation	260	9.6	0.53	1.3	[118]
Chemical plating	Vacuum evaporation	500	10	0.5	2.5	[113]

Reddy et al. have produced a glass/ SnO₂:F/SnS/CdS/In solar cell with a much improved efficiency of 1.3 %. This device used SnS layers produced by chemical spray pyrolysis. The improvement in efficiency of this device was due to an improved J_{sc}=9.6 mA/cm² and an improved fill factor = 0.53 [118]. However, the open circuit voltage obtained on this cell was limited to 260 mV, this attributed to the low absorber layer thickness (0.6 μ m) used in these devices. Series and shunt resistance problems were observed in this device and they also contributed to the low efficiency observed. The junction had a quantum efficiency of ~ 70%. Fig. 15 shows the current-voltage characteristics of this cell.

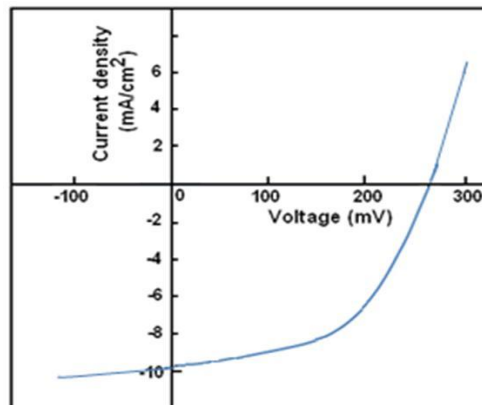


Fig. 15. I-V Characteristics of CdS/SnS junction.

SnS layers grown by chemical plating were used by Ghosh et al. to fabricate solar cells using vacuum evaporated CdS as the window layer. The device has so far showed the highest efficiency for SnS device obtained to date (2.5 %), with open circuit voltage as high as 500 mV [113]. The high series resistance and low response in the high energy side are considered to be limiting the device efficiency. Electrochemically deposited SnS layers were used by Gunasekaran and Ichimura to produce CdS/SnS and CdZnS/SnS heterojunctions. The solar cells fabricated with $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($x=0.13$) had efficiencies than those produced with CdS window layers. The former junction had $V_{oc} > 288$ mV and $J_{sc} > 9.2$ mA/cm², better values than those that resulted in an efficiency of 0.7 % [116]. Although the open circuit voltage and short circuit current density are comparable with the reported values, the efficiency is mainly limited by the low value of the fill factor (0.3). The authors attributed the poor performance to low minority carrier diffusion length and the interface states at the junction. Avellaneda et al. fabricated SnS-based photovoltaic cells with the configuration glass/SnO₂:F/CdS/SnS/(CuS)/Ag using all chemcially deposited layers. Although they produced cell with $V_{oc} > 400$ mV and $J_{sc} > 1$ mA/cm², the V_{oc} decreased with an increase of J_{sc} when heat treating in air at 423 K. The best cells had an open circuit voltage of 340 mV with a short circuit current density of 6 mA/cm² [118]. ZnO/SnS heterostructures were also developed using all electrodeposited layers. Although they exhibited photovoltaic behaviour, the device efficiency was very low [31]. Li et al. have produced p-SnS/n-Si solar cells using chemical bath deposited SnS films [112]. These devices had $V_{oc} > 480$ mV, $J_{sc} > 8.86$ mA/cm² with a conversion efficiency of 0.7 %. They also developed n-CdS/p-SnS and nZnO/p-SnS junctions and investigated their performance. The conversion efficiencies obtained in these junctions was very low; however, in some of the CdS/SnS devices J_{sc} values > 13.2 mA/cm² were obtained.

6. Conclusions

Thin films of SnS have now been produced by a range of methods and investigators reported how the chemical and physical properties of the SnS layers deposited vary with the deposition conditions used. Several independent research groups have also investigated the electrical and electro-optical properties of the junctions made with CdS. It is interesting to note that despite the junctions being far from optimum, photovoltaic activity has been observed in most of the devices. This is despite the layers used being far too thin to absorb most of the incident light.

The highest efficiency device developed to date was produced with an efficiency of 2.5 %. The series resistance of the device was found to be $\sim 10 \Omega$, high enough to be limiting the device efficiency. In addition, since the films were grown by a chemical method, the thicknesses of the layers used were probably less than the minimum thickness needed for light absorption ($1.5 \mu\text{m}$). Increasing the SnS thickness to $> 1.5 \mu\text{m}$ will increase the cell efficiency in 3 ways :

- (i) It will ensure the absorber layer is thick enough to absorb most of the incident light. [As $I = I_0 \exp(-\alpha d)$, an optical absorption length $1/\alpha = 1 \mu\text{m}$ for $\alpha = 10^5 \text{ cm}^{-1}$].
- (ii) It will ensure that the film thickness is big enough to support the depletion region width in the SnS absorber layer. [If the depletion layer and back contact overlap then V_{oc} at the junction will be reduced].
- (iii) When the film thickness is increased, the grain size will be increased, reducing the chance of recombination at the grain boundaries. [This will increase the short circuit current].

The growth of thicker films of SnS has now been achieved and work in progress to improve device efficiencies. Given the very limited work worldwide on this material system the results

are very promising, roughly comparable to the performance of the best organic solar cells fabricated to date.

It should also be noted that SnS and SnS₂ layers also have potential to be used as Cd-free buffer layers in copper indium gallium diselenide and copper indium disulphide solar cells. The CdS layers usually used are very thin (50nm thick) deposited using chemical bath deposition. The most promising materials investigated so far to replace the CdS are ZnS, In₂S₃ and MgZnO. Of these the former two materials have performed the best. However the lack of abundance of In makes ZnS as the front runner to replace the CdS. SnS and SnS₂ have the advantage over ZnS that they are much more conductive than ZnS, minimising series resistance problems in the heterojunctions formed. These materials may also be used with the more novel chalcopyrite materials currently being developed to minimise the use of Ga and In e.g. CuAlInSe₂ and Cu₂ZnInSe₂. Work to assess the potential of SnS and SnS₂ buffer layers for all these applications are currently in progress.

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